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The Influence of Mixing Water on the Thermophysical Properties of Nanofluids Based on Solar Salt and Silica Nanoparticles

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Abstract. The use of nanofluids (NFs) based on Solar Salt (SS) and nanoparticles (NPs), either as Thermal Energy Storage (TES) material or as Heat Transfer Fluid (HTF), is attracting great interest in recent years. Many authors [1,3] have reported important improvements on the thermophysical properties (specific heat capacity c_p,thermal conductivity k) of NFs based on SS and ceramic NPs. These improvements would lead to important savings and better performance of TES facilities on new Concentrated Solar Power (CSP) plants due to lower quantities of material required and smaller storage tanks. To achieve these advantageous features in the final NFs, it is essential to avoid NP agglomeration during their preparation. Different synthesis procedures have been reported: mixing of solid NPs within a SS solution by means of ultrasounds [1-3], direct mixing of solid NPs and molten salt [4]. In this work, NFs based on SS and 1% by wt. of silica NPs were synthetized from a SS-water solution and a commercial water-silica NF called Ludox HS 30% (Sigma-Aldrich). The influence of the *mixing water* volume (MW) on the c_p of NFs was evaluated. With this aim, the c_p of these samples was measured by Differential Scanning Calorimetry (DSC) both in the solid and the liquid state. In addition, the distribution of sizes was measured during the whole preparation process by Dynamic Light Scattering (DLS). Further information about sizes and uniformity of the final NFs was obtained from Scanning Electron Microscopy (SEM) images. X-ray Diffraction (XRD) patterns of the SS and final NF were performed.

INTRODUCTION

CSP plants require more and more efficient TES in order to supply energy during nights or cloudy periods. When using SS as TES material or HTF, an enhancement in c_p would lead to important savings in the cost of the whole process. The use of SS-based NFs is attracting great interest in recent years. Different authors [1-3] have reported an increase in the c_p of SS by addition of a small amount of NPs. The dispersion of NPs within a base fluid is known as *nanofluid* (NF). The most employed method for preparing salt based NFs consists of three steps: (1) mixing solid salt and NP, (2) adding water, (3) sonication and (4) drying. Sonication helps to achieve nanometric sizes and a uniform mixture. Other authors [4] have directly mixed the NPs within the molten nitrate salt under stirring. Table 1 shows the method of preparation and the total amount of water in every case.

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TABLE 1. Preparation methods for different authors and the total amount of water used (mL/g). Enhancements of c_p with respect to the base salt were comprised within 19 and 34% in the liquid state for the different authors. NP: nanoparticles, US: ultrasounds

Author	Year	Salt composition (% w/w)	NP conc. (% w/w)	Method of preparation	Total amount water (mL/g NF)	Ref.
Chieruzzi et al.	2013	$NaNO_3$ (60%) + KNO_3 (40%)	SiO_2, Al_2O_3 TiO_2 (0.5 – 1.5%)	Salt + NP + water US and drying	100	[1]
Shin and Banerjee	2011	$BaCl_2$ (34%) + NaCl (13%) + $CaCl_2$ (40%) + LiCl (13%)	SiO_2 (1%)	Salt + NP + water US and drying	100	[2]
Andreu-Cabedo et al.	2014	$NaNO_3$ (60%) + KNO_3 (40%)	SiO_2 (0.5 – 2.0%)	Salt + NP + water US and drying	10	[3]
Ho and Pan	2014	$NaNO_3$ (7%) + KNO_3 (53%) + $NaNO_3$ (40%)	Al_2O_3 (0.016 – 1%)	Adding NP within melted salt under stirring	---	[4]

An adequate control of the distribution of NP sizes during the preparation steps is essential to achieve an improvement of the c_p for the final NFs. The higher the NP available surface (S_a) in the molten salt media, the higher the interaction between the NPs and the ions within the molten medium. A high S_a can be only achieved by keeping particle sizes at the nanometric scale (<100 nm). Therefore, agglomeration and sedimentation of NPs must be avoided. During the preparation of NFs, water can prevent the agglomeration of NPs by maintaining them adequately solvated. However, two factors may be taken into account: on one hand, the more the total amount of water, the less the agglomeration of NPs. On the other hand, from the point of view of technical and economic feasibility, the use of big amounts of water will increase the overall cost of the process. A commitment between these two factors must be reached. The lowest amount of water that guarantees the good performance of final NFs at a reasonable industrial cost must be used.

In this work, a novel procedure for preparing SS-based NFs is proposed starting from a water dispersion of NPs, rather than from solid NPs (as those exposed in Table 1). A thorough control of the distribution of sizes was performed in order to achieve NFs with enhanced c_p. A correlation between the distribution of sizes for the NFs (in terms of S_a) and the c_p was found. The influence of the total amount of water on the distribution of NP sizes and the c_p of final NFs was analyzed. It is worth mentioning that NP have natural tendency to form clusters and agglomerates in the molten salt in the long time but maintaining the initial NP sizes as smaller as possible will delay this trend. The present research is important to establish a reliable, economical and scalable manufacturing process of high temperature nanofluids.

EXPERIMENTAL

Synthesis procedure

Materials

The materials used for the synthesis of NF were the following: sodium nitrate (SQM, Industrial grade, prills), potassium nitrate (HAIFA, Multi-K, prills) and Ludox HS 30%, a commercial colloidal dispersion of silica NP in water provided by Sigma-Aldrich. All the chemical products were used as received.

Preparation of Solutions

SS was prepared by mixing 60% w/w sodium nitrate and 40% w/w potassium nitrate, followed by melting at 450ºC for ½ hour to ensure the homogeneity of the mixture. Starting from this SS, two aqueous solutions were

prepared: 15% w/w and 50% w/w (SS/water). As the second concentration was near the saturation limit, SS was slowly added to warm water (about 50ºC) under smooth stirring.

A diluted dispersion of silica NP of 1% w/w was prepared by simple dilution of Ludox HS 30% with alkaline water at pH 9 (The pH of water was set at 9 with NaOH).

Preparation of Nanofluids

SS-based NFs were prepared following the scheme shown in Fig. 1:

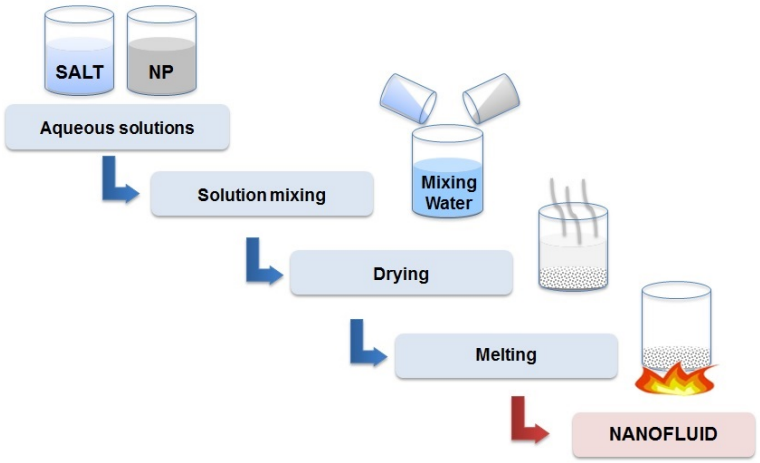


FIGURE 1. Preparation of NFs

Many variables can be modified during this preparation procedure (drying and melting temperature and time ..). A complete study of these variables would be of interest, but it is beyond the scope of this paper.

The amount of Mixing Water (MW) in the solution mixing step (Fig. 1) is a variable of great importance to control the degree of agglomeration. Water coming from salt solution and NP dispersion was also considered in the total amount of water. During the preparation of NFs, an adequate grade of solvation will prevent silica NP from agglomeration.

Starting from a solution of SS 15% w/w and a diluted dispersion of silica NP at 1% w/w, two trials were performed: (1) with MW 25 mL and (2) with no MW. In an attempt to set the water content to a minimum, an additional trial was done, starting from SS 50% w/w and Ludox HS 30% with no MW (3). The order of addition in the trial 1 was the following: first the silica dispersion and second the nitrate solution. Both solutions were added within the initial MW. For the trial 2 and 3, the silica dispersion was added directly into the nitrate solution, as no mixing water was used. The additions were performed, all at once, and under smooth stirring.

Drying was performed inside an oven (trade Raypa), at 100ºC in a glass Petri dish of 150 mm x 30 mm (diameter x width), covered with a filter paper, for the needed time to complete drying of the sample. Drying volume was the same for the three trials. All samples were dried in the same conditions. Melting was performed in a furnace (Nabertherm) at 450ºC for ½ hour. After melting, all samples were rapidly cooled at room temperature until their complete solidification.

Characterization

Dynamic Light Scattering

During the synthesis procedure shown in Fig. 1, monitoring of the NP sizes was performed by Dynamic Light Scattering. For this purpose, a ZetaSizer nano ZS, supplied by Malvern Instruments (UK) was used. Prior to the measurement, a dilution of the sample at a concentration of 0.1 g/L was done, in agreement with Malvern experts' advices. The S_a of the dispersed NPs was calculated considering that NPs were spherical, according to DLS measurement assumptions.

Scanning Electron Microscopy

The dispersion of NPs in the solid samples was evaluated using a field emission Scanning Electron Microscope SEM (JEOL, 7001F). Specimens were metallized in a thermal evaporator. Secondary Electron (SE) and Quadrant Back Scattering Electron Detector (QBSD), attached to an Energy Dispersive X-Ray Spectroscopy system (EDX) were used to measure the size and composition of NP clusters in the solid salt.

X-Ray Difraction

A XRD device Bruker D8 Advance was used to evaluate the crystallinity of the samples. XRD patterns of the SS and SS doped with silica NPs from the three trials were taken.

Differential Scanning Calorimetry

A DSC device TA Instruments Q100 (US) was used to measure the specific heat (c_p) of the different samples through Modular Differential Scanning Calorimetry (MDSC) with an isothermal procedure. Three temperatures, 196ºC (solid state), 256ºC and 396ºC (liquid state) were tested. Some milligrams of the sample were introduced in a pan and then hermetically sealed. All the samples were first stabilized at the desired temperature, and then subjected to an isothermal period of 10 minutes in order to achieve the salt thermal equilibrium prior to data collection (20 minutes). The modulation was set up with 0.6ºC of amplitude and a 110 seconds period according to the TA Instruments expert advices. The explained isothermal program was always performed from the highest to the lowest temperature. Thus, a complete melting of the sample was achieved at the beginning of the experiment (melting temperature 220ºC). In this way, the sample within the crucible in the solid state behaves as a compact piece rather than the initial fine powder. First, the sapphire sample commonly used as the reference material was measured under the same protocol to find out the possible device divergence and correct the final sample results. Three replica were measured for each sample. The average and the standard deviation (SD) for the three measurements were obtained. Results were discussed in relation to the degree of agglomeration and the preparation procedure for every sample.

RESULTS AND DISCUSSION

Preparation of Samples

All the samples (trials 1, 2 and 3) were prepared as shown in Fig. 1. Table 2 shows the total amount of water per gram of final NF, including MW and water from the starting SS solution and NP dispersion.

TABLE 2. Preparation conditions for Trials 1 to 3.

Trial	Initial solutions		Solution mixing		Final sample
	SS conc. (% w/w)	NP conc. (% w/w)	Mixing Water MW (mL)	Total amount water (mL/g NF)	NP conc. (% w/w)
1	15	1	25	31.60	1
2	15	1	0	6.50	1
3	50	30	0	0.97	1

Dynamic Light Scattering

During the NF preparation process, silica NPs tended to agglomerate. As a consequence, the distribution of sizes measured by DLS moved towards higher sizes. In Fig. 2, the distribution of sizes after every step of the preparation process is shown. From these curves, the global surface of interaction of NP (S_a) has been determined (Table 3). The higher this parameter is, the more effective the interactions between NP and the molten salt. Thus, larger improvements of specific heat may be reached.

In the Trial 1 (green line in Fig.2), NP sizes are the same on the initial silica dispersion and after the addition of nitrates (S_a=1.02 m^2/g, Table 3). In this sample, the raw silica dispersion was first diluted to 1% w/w and then added to 25 mL of MW containing the nitrates under stirring. There is plenty of water to maintain silica NP in suspension without agglomeration. However, a noticeable change is observed in the drying step and the S_a is reduced by 10

times after the recovery of the solid sample (S_a=0.12 m^2/g,). During this process, water is coming out of the solution and NP clustering and agglomeration occurs because the electrostatic interactions between them in the solid state. Once the nanofluid has been melted, it seems that these clusters are broken because the S_a is folded by two (S_a=0.25 m^2/g). The most probable reason is the loss of intramolecular water from silica NP as well as surfactants contained in the commercial silica dispersion employed as raw material. The temperature applied during the drying step (100 ºC) is very low to produce these changes.

The size distributions of Trial 2 (blue line in Fig. 2) are quite similar to those found in Trial 1 and the exposed arguments are also valid. The difference is found analyzing the sample after the melting step. In this case, the S_a is equal to that measured in the dried sample (S_a=0.15 and 0.16 m^2/g, respectively). It would be expected an increase in the S_a, as observed in Trial 1, though no significant increase in S_a was noticed. The smaller NP surface of interaction of this sample in the final step is directly related with poorer results of its specific heat, at it is shown later.

Finally, the behavior of NP sizes through the synthesis procedure steps of Trial 3 (red line in Fig. 2) is analyzed. The agglomeration of silica NP once the nitrates have been added is noticeably (S_a=0.45 m^2/g) and larger than Trial 1 and 2. This follow the expected behavior in this sample, since there is not MW and initial solutions both of SS and silica NP are in high concentrations (50 and 30% w/w respectively). As a consequence, the scarcity of water molecules creates a competition between nitrate ions and silica NP to be surrounded by them. Despite this increase in NP size distribution, the S_a after the drying step is comparable to the other samples (S_a=0.17 m^2/g). The amount of water in Trial 3 is very reduced, which causes the sample to be dried quickly. The shortening of drying time led to a reduction of NP agglomeration. In the final nanofluid, the NP surface of interaction is very close to that on Trial 1 but a bit lower (S_a=0.23 m^2/g). This is an important result for the scaling-up of this method that would lead to considerable savings in production cost as the requirement of water can be reduced to a minimum.

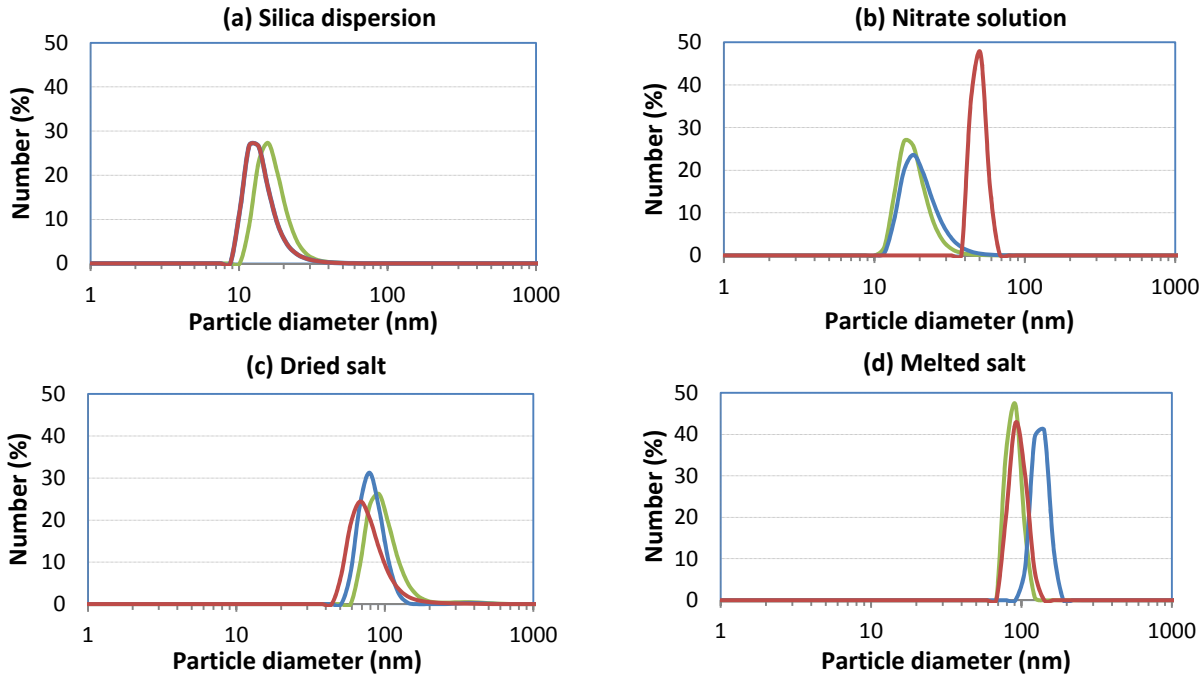


FIGURE 2. Distribution of sizes for the three samples of SS doped with silica NPs (— Trial 1; — Trial 2; — Trial 3). Preparation steps: (a) Solution mixing – Silica dispersion, (b) Solution mixing – Nitrate solution, (c) Drying, (d) Melting.

TABLE 3. Available particle surface (S_a) through the different synthesis steps.

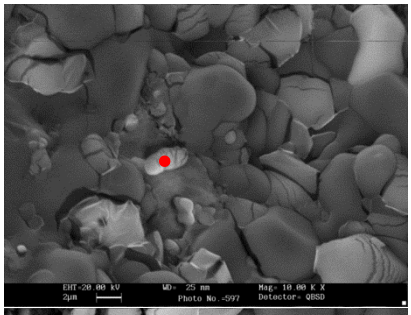
Trial	Preparation conditions		Available particle surface S_a (m^2/g)			
	Mixing Water MW (mL)	SS conc. (% w/w)	Silica dispersion	Nitrate solution	After drying	After melting
1	25	15	1.02	1.02	0.12	0.25
2	0	15	1.23	0.85	0.15	0.16
3	0	50	1.23	0.45	0.17	0.23

Scanning Electron Microscopy

Figure 3 shows SEM images for the three trials and EDX analysis. The differences in bright and contrast can be associated to changes in composition in QSBD images. Sodium (dark) and potassium (bright) nitrate crystals can be easily identified by variations in the grey tone. Silica NPs are distinguishable as a cotton-shaped structure, proved by the presence of silicon element. The EDX analysis covered an area of 1-5 μm^3, so it gave an approximate idea of the composition of the selected point, but X-Rays coming from adjacent areas were also captured. Oxygen was calculated by the software considering that the chemical compounds are oxides.

(a)

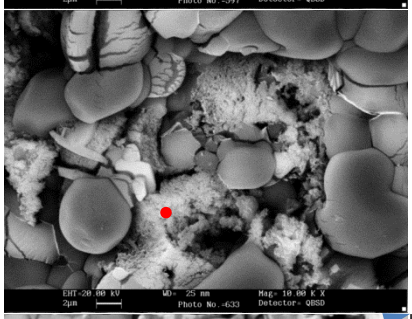
Trial 1



Element	Weight (%)
Si	11.06
K	62.48
Zn	0.87
O	25.59
Totals	100.00

(b)

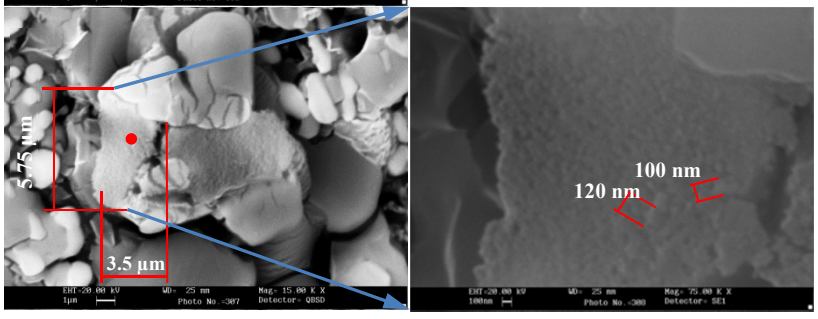
Trial 2



Element	Weight (%)
Na	17.25
Si	0.11
K	63.53
O	19.12
Totals	100.00

(c)

Trial 3



Element	Weight (%)
Na	11.24
Mg	3.36
Si	10.92
S	0.81
Cl	3.33
K	41.98
O	28.37
Totals	100.00

FIGURE 3. (a) Trial 1 QBSD image and composition EDX. (b) Trial 2: QBSD image and Composition EDX. (c) Trial 3: QBSD image and SE image with Composition EDX.

An estimation of the cluster size was performed for Trial 3 (Fig. 3c). The cluster seemed to be grouped in agglomerates of ~100 nm (Fig. 3). Clusters were probably divided into these agglomerates when solved in water.

Useful information about the uniformity and sizes of NPs has been obtained from SEM images interpretation. However, the SEM technique has only given an approximate idea of the agglomerate size distribution.

Differential Scanning Calorimetry

Table 4 shows the c_p and SD for the three trials at three temperatures (196ºC, 256ºC and 396ºC).

TABLE 4. c_p results for NF based in SS and silica NP in the solid (196ºC) and the liquid state (256ºC and 396ºC)

Trial	Preparation conditions		Specific heat c_p (J/g/ºC)		
	Mixing Water MW (mL)	SS conc. (% w/w)	196ºC (solid)	256ºC (liquid)	396ºC (liquid)
1	25	15	1.773 ± 0.014	1.627 ± 0.007	1.613 ± 0.004
2	0	15	1.289 ± 0.084	1.440 ± 0.083	1.384 ± 0.079
3	0	50	1.471 ± 0.033	1.620 ± 0.035	1.575 ± 0.034

Comparing the c_p values (Table 4) with the S_a calculated in Table 3, a relation between these two variables can be deduced, as shown in Fig. 4. The higher the S_a, the higher the c_p. This fact can be explained by the increase in the interactions between the surface of NPs and the nitrate salt media. There is not an important difference in c_p in the liquid state, 256ºC and 396ºC (0.4% and 2.4% respectively) between the trial 1 (0.25 m^2/g) and trial 3 (0.23 m^2/g). The difference in S_a between both trials is not high enough to affect the c_p in the liquid state.

Taking into account that preparation of trial 1 with S_a 0.25 m^2/g required a total amount of water of 31.6 mL/g NF and trial 3 with S_a 0.23 m^2/g required a total amount of water of 0.97 mL/g NF (Table 2), the total amount of water does not seem to affect the degree of agglomeration in the melting state. Final available surfaces are almost the same value for both trials, and moreover, the c_p values in the melted state are very similar in both cases. Therefore, the total amount of water can be reduced to a minimum during NF preparation, maintaining a good thermophysical performance of the final NF.

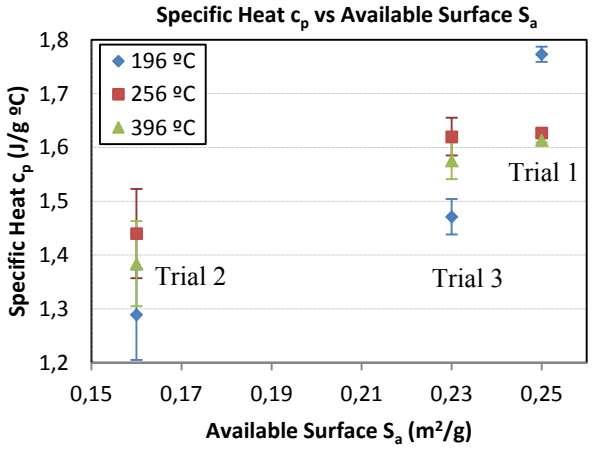


FIGURE 4. c_p (J/g ºC) vs S_a (m^2/g) for SS doped with NP of silica.

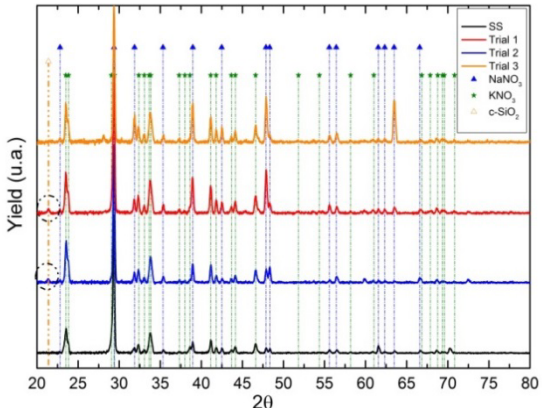


FIGURE 5. X-Ray diffraction patterns for Trials 1 to 3 and pure SS.

X-Ray Diffraction

Figure 5 shows the XRD diffractograms obtained for the three trials and the starting SS. The position of peaks (vertical lines) corresponding to $NaNO_3$ (blue lines), KNO_3 (green lines) and crystalline silica (yellow lines) are displayed in order to follow better the results. As it can be seen in Fig. 5, the three trials and starting SS show the sodium and potassium nitrate peaks, as it was expected. The differences in peak intensity are not relevant because

they could be related with random orientation of nanocrystals in powder samples, since the weight ratio of SS/silica is constant for the three trials (99:1). In addition, there is not peak broadening that can be associated with differences in the size of crystals. Although silica is usually in amorphous state, a small proportion of NPs are shown in crystalline way. As it can be seen, it shows a peak at 21° associated with crystalline phase SiO_2.

CONCLUSIONS

A novel method for preparation of NFs based in SS and silica NPs is exposed. The key feature of this procedure consists of starting from a stabilized water dispersion of silica NPs, rather than solid nanoparticles. In this way, the use of US is not required, as NPs are well dispersed and less agglomerated in the raw material. The preparation procedure consists of the following steps: (1) addition of silica dispersion, (2) addition of nitrate solution, (3) drying and (4) melting. The influence of the total amount of water on the distribution of sizes was evaluated. The nanoparticle sizes after drying does not seem to be affected by the total amount of water. Shorter drying times and therefore, less time for agglomeration, may be responsible of this fact. In the melting step, a general increase in S_a, and consequently decrease in NP sizes was observed. The final S_a was similar for the minimum total amount of water (0.97 mL/g NF) and the maximum one (31.60 mL/g NF): 0.23 and 0.25 m^2/g respectively. For economic reasons, the use of the minimum total amount of water is preferred (0.97 mL/g NF): no MW, starting from a nearly saturated SS solution (50%) and a non-diluted commercial silica dispersion called Ludox HS 30%.

The results from SEM analysis show that, in the solid state, nanoparticles are covering the nitrate crystals forming clusters of micrometric sizes. These clusters are formed by smaller agglomerates of ~100 nm in size. These results agree with the distribution of sizes measured by DLS, as clusters may be divided into nanometric agglomerates in water solution.

The higher the S_a (lower agglomeration), the higher the c_p of NFs. This can be explained by higher interaction surface between NPs and the molten salt medium. As stated in the previous paragraph, S_a was similar for the minimum and maximum total amount of water, 0.23 and 0.25 m^2/g respectively. In the liquid state (256ºC and 396ºC), the c_p of final NFs are also in the same order of magnitude, around 1.6 J/gºC. This means that the total amount of water can be reduced to a minimum with no effect on the final c_p of the NF.

NFs with very low degree agglomeration and adequate c_p to be used as TES materials can be prepared by means of the proposed method. The lower amount of water used with respect to other methods reported in literature, and the avoidance of US, would lead to lower fabrication costs at an industrial scale.

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